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MODIFICATION OF POLYMER OPTOELECTRONIC PROPERTIES
AFTER FILM FORMATION IMPURITY ADDITION OR REMOVAL

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SPECIFICATION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

10 The present invention relates to methods of making semiconductor devices using light emitting organic materials, and more specifically, to methods which involve the modification of the properties of an organic film after it has been deposited by either: (i) adding new components into the film from a top or bottom surface; or (ii) by causing components to leave the film from a top or bottom surface.

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RELATED ART

Polymers and blends of polymers and small organic molecules have recently been extensively used to fabricate organic light emitting diodes and thin film transistors.

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Organic films are typically deposited in thin film form for electrical and optoelectronic applications by uniformly coating a surface by spin-coating or other methods. Sometimes the final organic film itself is not directly formed, but a precursor is deposited which is converted to a polymer by a subsequent step, such as heating or exposure to UV light (e.g. PPV). It is also well known that adding various elements to the organic film can change its electrical and/or optical properties. These may include elements to change the conduction of electrical carriers (e.g. PBD for electron transportability), or dye centers to change the color of photo- and electro-luminescence (e.g. coumarin 6 in PVK). These extra elements are usually added to the original material before the final solid film is deposited. For example, these different groups could be bonded to a polymer chain before the polymer is deposited by spin coating, or may just be added as other polymers or individual smaller molecules to the solution containing the polymer before a thin film is formed. In either case all materials in the original solution become part of the final film.

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The goal of fabricating full color flat panel displays has the potential to be reached using organic light emitting diodes (OLEDs). The difficulty with using this technology is that the current deposition techniques, such as spin-coating and evaporation, deposit blanket films. The film can be used to make devices of a single color. To achieve individual emitters of different color next to each other, such as red, green, and blue, the deposited blanket film must be typically etched into a pattern, as might be done by photolithography followed by etching. Then, this process has to be repeated for multiple layers to achieve full color (red, green and blue emitters). Etching of organic films and photoresist processing for lithography on organic films has proven to be technically very difficult and expensive. Therefore, instead of making a blanket film of one color, etching and making a blanket film of another color, it would be beneficial to make one blanket film and later locally change the properties of the film to emit different light colors. Thus, the need for etching would be removed.

Another approach is ink-jet printing local regions, but a problem associated with ink-jetting printing is that the dots printed do not have a uniform thickness.

Accordingly, what is desired, and has not heretofore been developed, is a method to modify the properties of a film after it has been formed, by introducing therein or removing impurities to modify the properties therefrom.

OBJECTS AND SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for manufacturing optoelectronic organic films having locally modified areas.

5 Another object of the present invention is to provide an organic film with various regions of modified optoelectronic properties.

Still another object and advantage of the invention is to form an organic film with modified properties by applying dopants in desired places.

10 A further object and advantage of the invention is the provision of a method for forming an organic film with local modified areas by adding impurities to or removing impurities from the film.

Even another object of the invention is to provide a method for locally modifying properties of an organic film without the need for photolithography and etching of the organic film.

15 A still further object and advantage of the invention is the provision of a method for manufacturing a locally modified organic film with the need for contacting the surface of said film with solvents.

20 Even an additional object of the invention is to provide a process of forming a locally modified organic film wherein dopant is added to the film in an annealing process.

Yet an additional object of the present invention is to provide a process for transferring a dopant from one layer to another layer.

A further object of this invention is the provision of a process for transferring a dopant from one layer to another layer in a desired pattern.

25 The methods of this invention involve modification of the properties of an organic film after it has been deposited by either adding new components into it from its top or bottom surface, or by causing components to leave the film from its top or bottom surface. In the examples of these methods, the emitting color of light-emitting diodes are modified based on doped polymers by locally
30 introducing dopants causing different color emission into the film by local application of a solution containing the desired dopant to the film surface (by ink jet printing, screen printing, local droplet application, etc.). This overcomes difficulties encountered with the direct patterning of three separately formed

organic layers (each which uniformly coats an entire surface when formed) into regions for separate R, G, and B devices due to the sensitivities of the organic materials to chemicals typically used with conventional patterning technologies. Alternatively, dopants may be introduced in an organic film by diffusion from one layer into the film in local regions or by locally applying them directly into the organic film. Alternatively, dopants may be selectively removed from a film with solvents, etc.

Typically all of the active components are incorporated into the polymer when the polymer film is first formed, for example by spin coating it over a surface. In the present invention, the properties of the material are modified after a solid film has been formed by later introducing new species into the film from either its top or bottom surface, or removing impurities out through the top or bottom surface especially in a patterned arrangement. The method is especially attractive for the local modification of the photoluminescence and/or electroluminescence color of a thin film of the material, for example to create red, green, and blue light-emitting regions after a surface has been coated with a thin film of the material which is the same everywhere.

TOP SECRET

BRIEF DESCRIPTION OF THE DRAWINGS

Other important objects and features of the invention will be apparent from the following Detailed Description of the Invention taken in connection with the accompanying drawings in which:

FIGS. 1a and 1b are diagrams of the application of dye on top of PVK film.

FIGS. 2a and 2b are diagrams of dye on PVK film under UV illumination.

FIG. 3 is a plot of photoluminescence of materials used in **FIGS. 1-2**.

FIG. 4a is a diagram of a device and **FIG. 4b** is a plot of the electroluminescence spectra of PVK and C6.

FIGS. 5a and 5b are diagrams of removal of local dye with acetone.

FIG. 6a is a diagram of a device and **FIGS. 6b and 6c** photographs of the device of **FIG. 6a** under UV illumination.

FIG. 7 is a photograph under UV illumination of a device fabricated with an ink jet printer;

FIG. 8a is an experiment showing the effects of temperature on devices fabricated in accordance with the invention, and **FIG. 8b** is plot thereof.

FIG. 9 is a photograph under UV illumination of a device formed in accordance with the invention at increasing temperatures.

FIGS. 10a - 10c illustrate the steps in introducing film dopants from the top.

FIGS. 11a - 11c illustrate the steps in introducing dopants from the bottom.

FIGS. 12a -12c illustrates the steps for spatially modifying properties of polymer film.

FIGS. 13a - 13b illustrate the spectra of PVK and PVK with C6.

FIGS. 14a - 14c illustrate the steps in removing dopant from a polymer film into the underlying layer.

FIGS. 15a - 15c illustrate the steps in forming patterned addition of dopant from the top.

FIGS. 16a - 16c illustrate the steps in fabrication of patterned OLEDs.

FIGS. 17a - 17d illustrate the steps in fabrication of a passive matrix.

FIGS. 18a - 18c illustrate the steps in removal of dopant from polymer film in a pattern to the underlying layer.

5 **FIGS. 19a - 19b** illustrate the steps in removal of dopant from the top of a film.

FIGS. 20a - 20c illustrate the steps in the patterned removal of dopant from the top of a film.

10 **FIGS. 21a - 21d** illustrate the steps in fabrication of an active matrix OLED display.

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DETAILED DESCRIPTION OF THE INVENTION

The goal of fabricating full color flat panel displays has the potential to be reached using organic light emitting diodes (OLEDs). The difficulty with using this technology is that the current deposition techniques, such as spin-coating and evaporation, deposit blanket films. The film can be used to make devices of a single color. To achieve individual emitters of different color next to each other, such as red, green, and blue, the deposited blanket film must be typically etched into a pattern, as might be done by photolithography followed by etching. Then, this process has to be repeated for multiple layers to achieve full color (red, green and blue emitters). Etching of organic films and photoresist processing for lithography on organic films has proven to be technically very difficult and expensive. Therefore, instead of making a blanket film of one color, etching and making a blanket film of another color, it would be beneficial to make one blanket film and later locally change the properties of the film to emit different light colors. Thus, the need for etching would be removed.

The present invention, in a broad, general sense, relates to the application of an organic film and thereafter modifying local characteristics thereof by adding or removing components, i.e. dopants, dyes, etc., to or from the film to change the local characteristics of the film. Specifically, the invention relates to modifying the optoelectronic properties of an organic film by impurity or additional removal in a patterned fashion after application of the film. Even more specifically, the invention relates to modifying the emitting color of light-emitting diodes based on doped polymers by locally introducing dopants causing different color emission into an organic film by local application of solutions containing desired dopants to the film surface, i.e. by ink-jetting or screen printing. Alternatively, impurities contained within the film prior to application can be removing therefrom in desired patterns through various methods such as by the application of solvents.

One way for achieving this result is to locally dye a poly(9-vinylcabazole) (PVK a hole transporting polymer) spun-on film, with green, red and blue dyes. The dyes would dissolve in acetone or trichloroethylene (TCE), solvents that do not dissolve PVK, and could be patterned on top of the PVK film using an ink-jet printer. As shown in **FIGS. 1a** and **1b**, the dopants diffuse into the film and the

solvent evaporates. Then metal cathodes could be patterned on top of the locally dyed regions, thus achieving full color integration.

To verify this technique, droplets of coumarin 6 (C6, a green dye) dissolved in TCE and Acetone were placed onto a spun-on 1000 angstrom thick PVK film using a pipette and the solvents were given time to evaporate. **FIG. 2a** shows a picture of these drops taken from above with a UV lamp shining on them to excite fluorescence of the organic film. Under UV, they appear to be a greenish yellow color. These droplets were also placed onto glass where no diffusion occurs and the C6 remains on the surface, and the solvents were allowed to evaporate, as shown in **FIG. 2b**. Under UV lamp they appear to be a reddish color. This indicates that when the drops are placed onto a PVK film there is some interaction with the PVK, because when the PVK is present the dyed areas appear greenish-yellow, and when the PVK is not present the dye appears red. The interaction is the diffusion of the dye into PVK.

In order to state the above observations in a more quantitative way, a photoluminescence spectra was taken. **FIG. 3** shows the PL spectra of a pure PVK film (peak at 410 nm), a PVK film locally dyed with C6 (peak at 490 nm), a blend film, where the PVK was dyed in solution with C6 (peak at 490 nm), and the dye on glass (peak at 580 nm). This provides evidence that not only does the dye interact with the PVK, but it interacts in such a way that the PL spectra is nearly identical to that of a blend film, which is known to be able to be made into a device. Therefore, the next step was to attempt to make a device using this locally dyeing procedure.

FIG. 4a shows the device structure, and **FIG. 4b** shows the electroluminescence (EL) spectrum of the device and the EL of a blend device made by dissolving PVK and C6 in chloroform, spinning the film, and evaporating contacts. To make the locally dyed device, PVK dissolved in chloroform was spun onto glass coated with indium tin oxide (ITO, a transparent conductor). Next, a drop of C6 dissolved in acetone was dropped onto the surface, the sample was then spun again. Finally, a metal contact was evaporated on top of the dyed area. The EL spectra of the locally dyed device is seen to have the same 490 nm peak as the blend device. Therefore, this shows that the dye not only interacts

with the PVK, but it interacts in such a way that a device can be made which has a similar EL spectra to blend device.

In order to further investigate this locally dyeing phenomenon, an experiment was set up to see if dye could be washed out of a blend film, which had been dyed in solution. **FIG. 5a** and **5b** shows a schematic of the experiment. First, PVK and C6 were dissolved in chloroform. Next, they were spun-on to an ITO coated glass substrate, forming a 1000 angstrom film. When this film was observed under a UV lamp, it appeared green. Next, a drop of acetone was dropped onto the surface. When a UV lamp was shone onto the sample, it was observed that where the drop of acetone had been, the sample was blue, and where it had not been, the sample was green. This indicates that the dye could be washed out of a blend film, which created a local area without dye. Therefore, two different color LEDs could be made on a substrate which had been locally washed.

FIG. 6a shows a schematic of the device made on the washed film. The film was prepared as mentioned above, and then metal cathodes were evaporated in the washed areas and in the non-washed areas. These cathodes were thermally evaporated and were patterned by a shadow mask. **FIGS. 6b** and **6c** are pictures of the devices, from below, emitting light. **FIG. 6b** shows a device emitting green (appears light blue because of camera used) and **FIG. 6c** shows an emitting blue. The green device is emitting green because the metal cathode was evaporated on top of the dyed film, and the blue device is emitting blue, because the metal cathode was evaporated on top of the washed film.

Thus, devices can be made by locally dyeing a PVK film, or by locally washing a dyed PVK film. Therefore, the next step is to pattern the dye using an ink-jet printer. **FIG. 7** shows a picture of a piece of glass coated with ITO, onto this glass was spun a 1000 angstrom thick film of PVK. Then an Epson Stylus Color 400 ink-jet printer was used to pattern C6 dissolved in acetone on top of the film. The sample was then illuminated under UV. This shows that the dyes can be patterned by an ink-jet printer with a spot diameter of $\sim 500 \mu\text{m}$. The next step is to try to determine the ultimate resolution of this technique.

An experiment was done to determine if the diameter of the printed spots could be influenced by temperature. **FIG. 8a** shows the experimental set-up, a 1000 angstrom film of PVK was spun onto a piece of glass coated with ITO. The sample was then placed onto a hot plate. Droplets of equal volume of C6 dissolved in acetone and equal volumes of C6 dissolved in TCE were dropped on to the PVK film at different temperatures. It was observed that at higher temperatures the spots did not spread as far and therefore had smaller diameters. This is shown in the plot of **FIG. 8b**. This could potentially make the spot size ~0.6 times smaller. However, this data does not reveal the difference observed in using TCE and acetone.

FIG. 9 shows a picture of the same spots dropped onto the PVK film at increasing temperatures lit up by a UV lamp. What can be seen is that there are, at higher temperatures in the TCE drops, bright yellow spots which are ~ 1/3 of the outer spot, and have a more intense luminescence. This may be because, as the solvent dries the C6 tends to stay in the solution and what is left at the end is a highly concentrated small diameter spot. When this spot profile is checked using a surface profilometer it is seen that the dye is actually sitting on the surface. Therefore, in order to take advantage of this small diameter, the substrate would have to be heated further, to allow the dye to thermally diffuse into the film.

In conclusion, PVK can be locally dyed by dissolving dye in acetone or TCE and dropping it on to the surface. Also, this dyed area can be made into a device. A blend film of PVK and C6 can have the C6 locally washed out of it using acetone, and a device can be made using this technique. At the present time ink-jet printed dyed lines can be made with widths of ~500 μm . This width can be further reduced by printing with TCE onto a heated substrate to obtain a spot 1/10 of the diameter of a spot made at room temperature. This substrate would have to then be heated again to thermally diffuse the dye into the film.

FIGS. 10a-10c illustrate the basic method for introducing film dopants from the top in the fabrication of red, green and blue OLED devices on a common substrate. As shown in **FIG. 10a**, a uniform film of polymer 10 without the desired dopant is formed on substrate 11. The polymer film 10 may contain other

dopants. In **FIG. 10b**, dopant 12 is placed on the surface of the polymer film 10 by evaporation, spin coating, or other method. In **FIG. 10c** annealing or other process caused the dopant 12 to enter the film 10 by diffusion or by other methods. The solvents used in spin coating the dopant 12 on the surface may cause dopant 12 to enter polymer 10 and be deposited into it without need for the steps described in **FIG. 10c**. In this case there is never a solid dopant layer on the surface.

FIGS. 11a-11c show the introduction of dopants into a film from the bottom thereof. In **FIG. 11a**, a substrate 13 has a coating 14 put down thereon. The coating 14 may contain the desired dopant or, the dopant may be applied in the manner described in **FIGS. 10a-10c** (i.e. may be polyaniline or similar hole transport layer in OLED). As shown in **FIG. 11b**, the polymer film 15 is deposited onto the coating 14. In **FIG. 11c**, annealing causes dopant to partially migrate from layer 14 into polymer film 15. It should be noted that the solvents used in spin coating the top polymer may "leach" dopant out of the underlying layer without the need for the thermal cycling described in **FIG. 11c**.

FIGS. 12a-12c show the steps of a method for spatially modifying the properties of the polymer film. **FIG. 12a** illustrates the deposition of a polymer 16 onto a substrate 17 in the same manner as discussed in connection with **FIG. 10a**. **FIG. 12b** shows the creation of local regions of different dopants, 18 and 19 on the polymer surface 16 by local deposition methods such as evaporation through different shadow masks, deposition by screen printing using different screens, or by ink jet printing, or other printing processes using different patterns for each dopant. **FIG. 12c** illustrates the heat treatment of the structures of **FIG. 12b** by annealing, for example, to cause the dopant 18 and 19 to migrate into the polymer 16. As discussed in connection with **FIGS. 10a-10c**, solvents used in screen printing or in ink jet printing may carry dopants directly into the polymer so that the heat treatment step of **FIG. 12c** may not be required.

This has been demonstrated using dyes C6 (green), C47 (blue), and Nile red (green) in acetone solution separately applied to individual regions of a single PVK film, where acetone solution is locally applied by an eyedropper or similar device. Acetone does not cause removal of PVK film, but after evaporation of

acetone in a few seconds the fluorescence color of the film under UV excitation has changed.

As illustrated in **FIGS. 13a-13b**, both the photoluminescence (**FIG. 13a**) and electroluminescence (**FIG. 13b**) show the shift between pure PVK film and doped PVK.

The dopant need not be pure dopant, but may be co-deposited with another material. Subsequent process (or the very deposition process itself) can then cause dopant to move into underlying layer. Other material may be removed or remove itself (evaporate), or stay behind as separate layer and be part of final structure doped or undoped.

The spatial variations of **FIGS. 12a-12c**, may be applied to the method described in connection with **FIGS. 11a-11c** so that patterns of dopant may be introduced into underlying material before top polymer film is deposited.

FIGS. 14a-14c illustrate the steps in the removal of dopant from polymer film into an underlying layer. In **FIG. 14a**, substrate 19 has a bottom absorber film layer 20 deposited thereon. The absorber layer has a low chemical potential for the desired dopant. In **FIG. 14b**, the doped polymer 21 is deposited onto the absorber layer 20. In **FIG. 14c**, annealing or another cycle which causes the dopant to move is applied. In lieu of the heating treating, a solvent may be applied which infiltrates (from the top) both the polymer layer 21 and the bottom layer 20 to enable the dopant in the top polymer layer to migrate into the bottom layer 20.

FIGS. 15a-15c shown the patterned addition of dopant from the top with an impermeable barrier. In **FIG. 15a**, the undoped polymer 23 is deposited on substrate 22. In **FIG. 15b**, a patterned layer impermeable by the dopant 24, 25, 26 is formed on the top of the polymer 23. In **FIG. 15c** dopant 27 in ambient is heat treated by annealing. Alternatively, the structure of **FIG. 15b** may be placed into a solvent containing the dopant

FIGS. 16a-16c illustrate the application of the method described in **FIG. 12** to the formation of patterned OLEDs of different colors. As shown in **FIG. 16a**, undoped polymer 30 is deposited everywhere onto ITO layer 29 on glass substrate 28. The ITO may be patterned. Local red (31), green (32) and blue (33) regions are formed by locally doping the polymer 30. These red, green and blue

regions may be formed by ink jet printing three different solutions in different regions. Heat treating may then be applied. In FIG. 16c, top contacts 34, 35, 36 are formed on the red, green, and blue regions by standard methods such as by evaporation through a shadow mask. In making OLED's applying color dopant by using localized solvent may change any dopants which were in film from original spin coating (e.g. PBD for electron transport). So, some of this dopant may need to be put in with the color dopant solution.

FIGS. 17a-17d illustrate the application of the method described in FIG. 12 to form a passive matrix color OLED display. In FIG. 17a, ITO lines 37 are formed in one direction on glass substrate 38. In FIG. 17b, a uniform polymer film 39 is applied over the ITO lines. In FIG. 17c, red, green, blue doped polymer 40 is formed on the ITO lines in the polymer film as by the steps described in FIG. 16b. FIG. 17d cathode lines 41 as top contacts perpendicular to the bottom contact lines 37. Doping need only be in the region of the intersection of the top and bottom contact lines.

FIGS. 18a-18c illustrate the removal of dopant from polymer film in a pattern to the underlying layer. In FIG. 18a, the absorber film 43 is deposited onto substrate 42. In FIG. 18b, absorber film 43 is patterned or coated with a patterned impervious layer 44. Doped polymer 45 is added onto the layer 44. FIG. 18c shows the effect of annealing or other treatment of the structure of FIG. 18b in causing the doping to move into the underlying layer 43, where it is not impeded by the impervious barrier. The movement of the dopant may be accomplished through the use of a solvent as discussed in connection with FIG. 14c.

FIGS. 19a-19b shows the removal of dopant from the top of an unpatterned film. In FIG. 19a, doped film 47 is deposited onto a substrate 46 as by spin coating with dopant in solution. FIG. 19b illustrates the treatment of the structure of FIG. 19a by annealing in certain ambients or washing with solvent to the cause the reduction of dopant in layer 47. Washing by applying the drop may not remove the dopant from the film, but cause it to move to the edge of the drop location, leaving little dopant in the center of the drop.

FIGS. 20a-20c illustrate the patterned removal of dopant from the top of the film. In FIG. 20a, doped polymer film 49 is deposited onto substrate 48. In

FIG. 20b patterned impermeable layer **50** is applied over the doped polymer layer **49**. In **FIG. 20c**, annealing the structure of **FIG. 20b** causes dopant to evaporate in areas without barrier **50**. This evaporation may also be accomplished by washing with solvent to remove dopant in the areas without barrier **50**, or
5 treating with a solvent vapor.

FIGS. 21a-21d show the formation of an active matrix OLED display. In **FIG. 21a**, glass substrate **51** has patterned insulator **52** and electrodes **53** formed thereon. The electrodes are connect to transistors (not shown) in the pixels. In **FIG. 21b**, undoped organic layer **54** is deposited everywhere on the structure of
10 **FIG. 21a**. In **FIG. 21c**, locally applied red (**55**), green (**56**) and blue (**57**) dopant is applied as by ink jet printing. As shown in **FIG. 21d**, top electrode **58** is applied without a pattern. Top electrode **58** may be, for example Al:Li or Mg:Ag cathode.

The methods described in this invention may be applied to any organic
15 film, not just polymer based. Solvent methods may cause problems with small organic molecule based films, however, dopants could be deposited by diffusion by thermal treatment by other localized methods such as evaporation through a mask, etc.

It should be further understood that "undoped" means not doped with the
20 dopant being added or removed. Other dopants may be present.

Having thus described the invention in detail, it is to be understood that the foregoing description is not intended to limit the spirit and scope thereof. What is desired to be protected by Letters Patent is set forth in the appended claims.